COMPUTER ANALYSIS OF GAMMA-RAY SPECTRA

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COMPUTER ANALYSIS OF GAMMA-RAY SPECTRA

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ABSTRACT

A computer program is being developed for application to rapid routine qualitative and quantitative analysis of complex gamma-ray spectra resulting from thermal neutron activation of samples of material having unknown composition, but a limited number of possible constituents (20 or 30 isotopes). Component identification is based on peak energy only, and stripping is accomplished using an isotopic spectral library on magnetic tape.

Various sections of the program have been largely completed, and results obtained in initial tests indicate satisfactory performance.

INTRODUCTION

When a sample of material is placed in a thermal neutron flux, most of the isotopes present will undergo nuclear reactions producing new species. Most commonly the reaction is of the radiative capture (n,γ) type, and in many cases the product nuclides are radioactive. These radionuclides will usually decay by beta emission with accompanying production of de-excitation gammas. Since each radionuclide will emit gammas at characteristic energies and with characteristic half-life, it is possible, by studying the gamma-ray spectrum of the material after neutron irradiation, to determine the identity and amount of each radionuclide produced during the irradiation. Since each radionuclide is formed from a particular natural isotope of an element, it should also be possible on the basis of known information to ascertain the elemental composition of the original sample.

This technique, thermal neutron activation analysis, is practical, and due to the extreme sensitivity with which radionuclides can be measured, is one of the most powerful and sensitive of all methods of elemental analysis. About 70 elements can be detected by this means in amounts as small as 10^{-6} to 10^{-12} grams, depending on the nuclear properties of the particular element of interest. In many cases this sensitivity far surpasses that attainable by any other means of analysis.

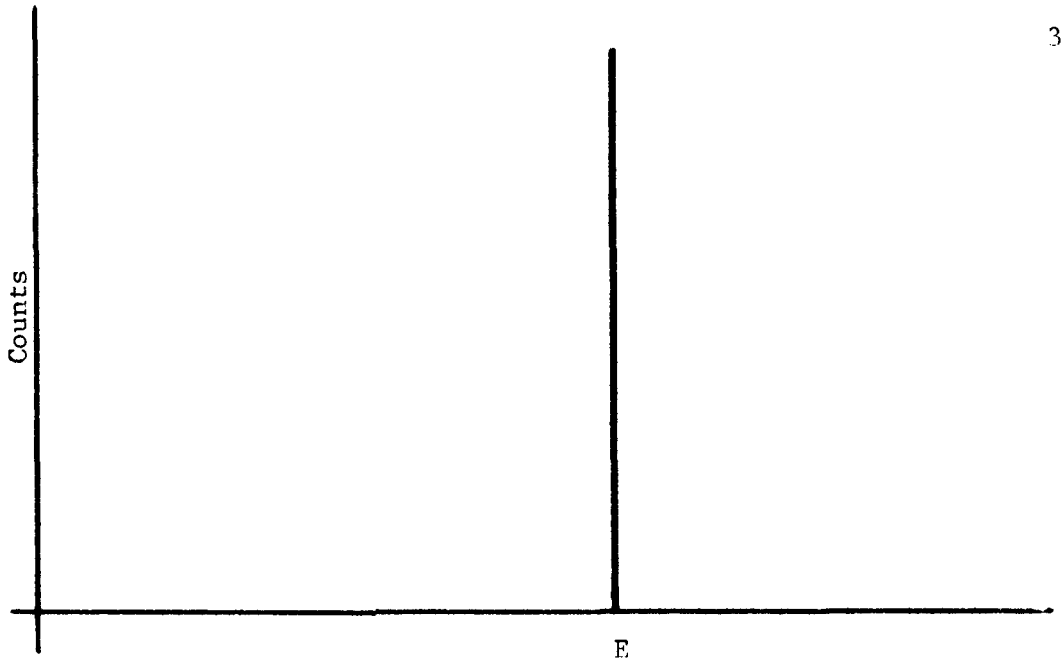
Unfortunately, this method of analysis is not without some disadvantages. Perhaps the most troublesome from a programming viewpoint, is the extremely complex nature of the data obtained from the

gamma scintillation spectrometer. Ideally, a spectrometer should present a monochromatic source of photons as a single line at the energy in question (Fig. 1a), a result which is closely approximated, for example, in optical spectrometry. However, due to the different modes by which a gamma photon may interact with matter and, in particular the scintillation crystal (photoelectric absorption, Compton scattering, pair production, etc.), the spectrum representing a monoenergetic gamma source of energy, E has an appearance such as shown in Fig. 1b, although the shape will vary considerably for different values of E (the detailed theory of gamma-ray spectrum formation may be found in the literature).[10,11]

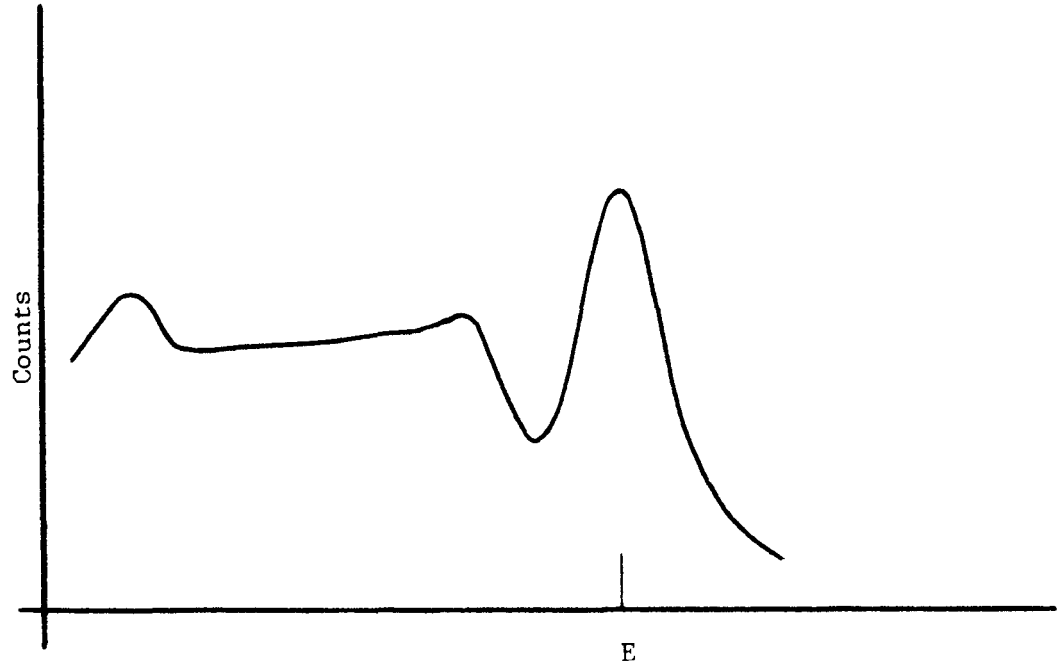
Since each radionuclide may emit gammas at several different energies, a composite spectrum due to several species may be quite complex. However, because of the great power and usefulness of neutron activation analysis, a great deal of effort has been brought to bear on the problem of processing such spectra to obtain the identities and amounts of the elements in the sample being analyzed with the greatest possible accuracy and reliability.

The Problem

The scintillation spectrometer records the number of pulses in each of a large number of channels which sort the pulses according to size (gamma energy) into M channels where the i^{th} channel corresponds to the energy range E_i to $E_i + \Delta E = E_{i+1}$. Usually $E_1 = 0$, and therefore E_{M+1} equals the total energy range covered by the spectrum. The spectrum is a discrete function, F(i), where F(i) is the total count in the i^{th} channel.



(a)



(b)

Figure 1

Comparison of the Responses of a "Perfect" Gamma Spectrometer and of a Real Scintillation Spectrometer to a Monoenergetic Source of Energy E.

The spectrum is assumed to be a summation of simpler spectra, each corresponding to a component radionuclide in the sample. The problem is to determine the identities and magnitudes of the component spectra present in the composite. In general, the qualitative analysis is made by measuring the peak energies and observed half-lives of the peaks. Once the identities of the constituents are known, standard spectra of pure known amounts of the corresponding isotopes are obtained and used to make the quantitative analysis by various comparison methods.

If $f_j(i)$ is the standard spectrum of the j^{th} isotope, then the composite spectrum is assumed to be a linear combination of the N standard spectra, i.e.,

$$F(i) = \sum_{j=1}^{N} a_j f_j(i) \qquad i = 1,2,\ldots,M \qquad (1)$$

where the a_j are the weighting constants relating the magnitudes of the standard spectra to the magnitudes of the corresponding component spectra in the composite, and hence to the quantitative composition of the sample. Since all variables related to the N standard spectra are known, once the constants a_j are determined, the spectral analysis is essentially complete.

Methods of Solution

The manual methods of processing gamma ray spectra do not attack the analytical problem directly due to the huge amount of calculation involved, but instead usually employ various graphical techniques[7,10] where the constants a_j are determined by making some type of area

measurement under corresponding peaks in the composite and standard isotopic spectra.

Unfortunately, in cases of practical interest these manual methods are usually extremely tedious and time consuming. Furthermore, even for simple cases there may be considerable error (2 to 5%), and for more complex spectra with, for example, 10 components these methods may break down completely due to complications such as overlapping or composite peaks, background, etc.

One obvious solution to the problem is the development of computer programs which will perform all or at least part of the analysis, and indeed this has been one of the primary areas of development in the field of activation analysis.

There are, of course, programs which use about the same techniques as are used for manual analyses but with some refinements made possible by the speed of the computer.[5] More commonly, however, the computer has been used to obtain a direct solution to the purely analytical program of spectrum unscrambling.

Notice that equation 1 is a set of M equations in the N unknowns, a_j, and further that M, the number of channels, is in general much greater than N, the number of component spectra present in the composite. This gives M - N degrees of freedom in the solution of the problem. Of course, it is easy to reduce the number of equations to N merely by adding some equations together and/or leaving some out, thereby making possible a unique solution by purely algebraic means. This is the basis of the method developed by Antila.[1] Even though this approach may seem undesirable because of the inherent destruction of information, it does offer certain advantages in some cases, as will be discussed later.

To obtain a solution to the full set of M equations (eqn. 1) in N unknowns, the method of least squares may be used. Define a residual spectrum:

$$R(i) = F(i) - \sum_{j=1}^{N} a_j f_j(i), \tag{2}$$

then

$$[R(i)]^2 = \left[F(i) - \sum_{i=1}^{N} a_j f_j(i) \right]^2 .$$

Now sum over all the channels,

$$\sum_{i=1}^{M} [R(i)]^2 = \sum_{i=1}^{M} \left[F(i) - \sum_{j=1}^{N} a_j f_j(i) \right]^2 . \tag{3}$$

Now, for the solution set, a_j, let this sum of the squares of the residuals be a minimum. Then, minimizing equation 3 with respect to a_k is equivalent to:

$$\frac{\partial}{\partial a_k} \sum_{i=1}^{M} \left\{ \left[F(i) - \sum_{j=1}^{N} a_j f_j(i) \right]^2 \right\} = 0 . \tag{4}$$

Equation 4, after some manipulation, leads to a set of N equations in the N unknowns, a_j, which is based upon all information available. This treatment is probably the best yet developed and has been extensively studied in the literature.[2,3]

For historic reasons the process of quantitative spectral analysis and subtraction of components to form a residual spectrum (such as defined

by equation 2) is known as stripping. The formation of a residual spectrum constitutes a useful check on the accuracy of the quantitative analysis, since in the ideal case it should be uniformly zero.

Up to this point, it has been assumed that the standard spectra, $f_j(i)$ are complete isotopic spectra. A different approach, however, has been developed by Heath and others.[4,6,8,9] The assumption is made that each isotopic spectrum (and hence the composite) is due to a collection of monoenergetic gamma components of various intensities and half-lives. Each standard spectrum, $f_j(i)$, is then a monoenergetic response function (resembling fig. 1b) which may either be generated by the program or be stored in a response library of some sort. A series of spectra are analyzed in terms of these monoenergetic spectra, thus obtaining a half-life for each component. The components are then grouped according to half-life and the members of each group summed in the proper proportions to obtain the isotopic spectra.

Objectives of the Present Work

At present most programs for routine spectroanalysis fall into two general categories. The more common type is designed to provide an accurate determination of the amounts of one or more elements known to be in the specimen by directly stripping the isotopic spectra of the constituents from the composite.

The second and more complex type is employed in the identification and quantitative analysis of samples of completely unknown composition. Since direct stripping of isotopic components would require a

large comprehensive library of standard isotopic spectra, the monoenergetic component treatment is usually applied.

The program now under development, which this report describes, deals with a particular type of analysis which seems to have been relatively neglected; namely, the analysis of samples whose composition is unknown but for which the number of possible constituents is limited (20 or 30 detectable isotopes). In such a case the need for a large comprehensive spectral library is avoided.

The identification of component isotopes is made on the basis of peak energies only. The isotopic spectra are then stripped using an isotopic spectral library. Half-life determinations are used to correct and refine the analysis.

The advantages of the method are its relative simplicity and directness and the fact that it permits a quick analysis of a single composite spectrum rather than requiring a long series of spectra for any results at all.

Also, an attempt has been made to make the analysis completely automatic in that no manual data manipulations or human decisions are involved in the analysis, thus making the results completely objective.

METHOD OF ANALYSIS

Experimental

In this research at the present time the spectrometer system used consists of a standard 2" x 2" NaI (Tl) well crystal coupled to a 1024 channel pulse height analyzer equipped with both printed tape and standard 8 channel perforated paper tape output. The perforated paper tape is converted directly to punched cards on a tape-card converter.

The computer facility used at this time consists of an IBM 7072-1401 system with a usable core storage of about 8000 words.

The samples are irradiated in a 100 kw TRIGA type reactor.

The specific problem being attacked in this research is the routine trace element analysis of particulate air pollution. The samples fulfill the requirement of having an unknown but limited composition, and because of the large number of samples to be analyzed, a completely automated method is highly desirable.

The Program

The complete analysis consists of a series of problems for which solutions are under development at this time. Some of the solutions are almost complete, while others are still in the early experimental stages. What follows is a general description of the program detailing these problems and methods of solution along with comparisons

of the methods with those already developed or under development by others. More detailed information on the mechanics of the program (flowcharts, listings, etc.) may be found in Appendix A.

Preliminary Processing

Before the analysis proper can begin, the raw gamma spectrum must undergo preliminary processing in preparation for component identification and stripping. The three main steps are:

1. data smoothing
2. peak location
3. energy scale calibration

The count in each channel of the spectrum is subject to statistical error which introduces a random variation of the spectrum from a smooth curve. This random variation or "noise" is not too serious if the energy per channel ratio is coarse (i.e., if the spectrum contains relatively few channels). In this research, however, a spectrum covering a range of about 2.5 MeV may be divided into as many as 1024 channels, giving an energy of about 2.5 KeV/channel. Even for ratios of the order of 15 KeV/channel, noise may be a rather serious problem when locating peaks and stripping.

It would be highly desirable, therefore, to enhance the spectrum to noise ratio by some analytical means while avoiding a loss of significant information.

One method commonly used for treatment of continuous numerical data is the technique of convolution. This method changes the value of each data point by considering a region of m data points on each side according to the equation

$$Y_j^* = \frac{\sum_{i=-m}^{m} C_i Y_{j+i}}{N} \quad . \tag{5}$$

Note that this equation considers a group of 2m+1 data points centered on the j^{th} data point and, using a set of 2m+1 convoluting integers, C_i and a normalizing factor N, yields a new value, Y_j^*, for the j^{th} data point, Y_j. The value, Y_j^*, is placed in a new data table. The entire spectrum is processed by letting j run through the channel numbers in the original data table.

This concept may be made more clear by noticing that if all the C_i's are equal to 1 and if N = 2m+1, the convolution simply represents a moving average of the ordinate values of the data points. The integers, C_i, are then simply a weighting function applied to the points on each side of a data point in determining its new value. Although many different sets of integer functions, C_i, have been tried, most result in some loss of information.

Perhaps the best possible results would be obtained by applying a least squares fit of a polynomial to the 2m+1 data points in order to determine a new value for the central point. This would seemingly entail a much more complicated procedure of setting up and solving a set of 2m+1 equations for each data point.

Fortunately, however, by making two simple assumptions (continuity of the spectrum and equal spacing of data points along the abscissa), this least squares polynomial fit can be shown[14] to be exactly represented by a set of convoluting integers, C_i, and a normalization factor, N.

The polynomial to be fitted may be parabolic, cubic, etc., and the value of 2m+1 (number of points in the fit) may be any odd integer above a minimum. A particular set of integers, C_i, and N is associated with each choice of a polynomial degree and a value of 2m+1 (tables of C_i and N may be found in ref. 14).

The question of the combination of polynomial degree and number of points per fit best suited for gamma scintillation spectra has been investigated by H. P. Yule[15] and also to some extent in this research. In general it has been found that a quadratic-cubic fit (the C_i's and N, are the same in both cases) with 2m+1 no greater than the width of a significant peak at half maximum gives the best results.

Once the spectrum has been processed to remove as much noise as possible, the program searches it for peaks. There may be many meaningless bumps and wiggles in the spectrum caused by the Compton effect, low frequency noise, etc. These must be discarded and only meaningful peaks which can pass statistical tests of validity should be recorded for analysis. Furthermore, the center of the peak must be located as exactly as possible in order to determine its energy.

The first step in this procedure is the generation of the first derivative of the spectrum. At present, to find the derivative at the j^{th} point, a linear least squares fit is made to the j^{th} point and the point on each side (3 points). The derivative is then just the slope of the line. Although this method is somewhat crude, it works surprisingly well.

This will soon be replaced, however, by a quadratic least squares fit on a region of perhaps seven points to obtain the derivative at the

central point in the region. It turns out[14] that this also may be exactly represented by a data convolution using a particular set of integers, C_i, and N. The convolution is performed directly on the unsmoothed data since the smoothing is accomplished by the fitting of the quadratic. This more sophisticated technique is expected to increase accuracy considerably.

After the derivative is obtained, the program scans it looking for changes of sign. A change from positive to negative may indicate a peak while the opposite change a valley. Of course, due to low frequency noise, etc., there may be many sign changes which mean nothing at all. Therefore, statistical tests are applied to ascertain the validity of the peak indication. Several types of tests have been proposed.[13,15]

The tests made by this program are based on two input parameters, p and h. To be admitted as a valid sign change, the derivative must have at least p successive channels with the same sign after a sign change. If the change is from positive to negative (a peak), the top of the peak must be at least h counts higher than the previous valley to qualify as a valid peak.

During the scan of the first derivative, the program first searches for a peak. Once a valid peak is found, a valid minimum is searched for, and so on until the last channel is reached. The values of p and h determine the minimum size of peak which is considered valid.

The sign change of the derivative provides a rough indication of the location of the center of the peak, but to obtain a more exact value, a linear fit is made to a region of the derivative centered on the apparent sign change and of width 2g, where g is an input parameter.

The intersect of the lienar fit with the abscissa is then interpreted to be the location of the center of the peak. Notice, however, that the center location of the peak does not have to be determined with great accuracy since on a steeply sloping background a peak center may shift as much as several channels. Accuracy within, for example, one-half channel would be ample.

Along with the channel number at peak center, it is useful to have some measure of the net height of each peak above background. Although this can be done in a variety of ways, the present method measures the absolute height of the peak (in counts) above the previous minimum.

In order to determine the energy of an unknown peak in a complex spectrum, it is necessary to know the energy-channel number ratio to a good degree of accuracy.

The usual method is to take spectra of known gamma standards (Co^{60}, Cs^{137}, etc.) before and after the unknown spectrum is formed. Then a manual plot is made of energy with channel number. The locations of the peaks (channel number) in the known spectra along with their energies are plotted as points on the graph, and a line through the origin is fitted to the points. This graph is then used to determine the energies of peaks in the unknown spectrum.

Both to facilitate data handling and to increase accuracy, this procedure has been incorporated as part of the program.

Several standard spectra taken just before or after the unknown spectrum are placed into the program input. Along with each standard spectrum a list of the energies of the known peaks and their approximate

locations (channel number with largest count) is included. The program then locates all peaks in each standard spectrum by the method previously described and proceeds to search through these detected peaks to find the ones corresponding to the standard peaks read in. A series of pairs of the form (x_i, E_i) is then formed where x_i and E_i are the location (channel number) and energy (MeV) of the i^{th} standard peak. The points are fitted by least squares to an equation of the form $E = kx$ where it is assumed that the E_i's are exact and the x_i's contain random errors. Having thus found a value of k it is easy to determine the energies of the peaks in the unknown spectrum by the use of the above relationship. This, then completes the preliminary processing.

Qualitative Analysis

The next major phase is the identification of components, i.e., the qualitative analysis. The program has available to it an isotopic spectral library on magnetic tape containing in addition to the spectra, other information associated with each isotope (see Appendix B for library format). Part of this information is a list of standard energies and relative heights of the peaks which characterize each isotopic spectrum.

On the basis of the peaks found in the unknown composite spectrum and the peak information in the spectral library, the program must decide which of the isotopes in the library are present in the composite. In principle, of course, the program just sorts through the peaks found in the complex spectrum to see whether the peaks corresponding to a particular isotope are present. There is a possibility, however, that a small

peak may be buried beneath a larger peak at a slightly different energy and remain undetected. The test for the existance of a particular peak in the composite involves, therefore, the examination of a relatively broad region taking into account other peaks present in the region and the relative sizes of these peaks and the one being searched for. The procedure yields a probability factor for the existance of the peak. These probability factors are used to make a decision regarding the presence or absence of a particular isotope.

An element in the sample will in some cases be composed of more than one isotope capable of being activated to a significant extent and so will form several radionuclides upon irradiation. In such a case an "indicator" radionuclide will be chosen from among those formed by the particular element. Ideally, the indicator radionuclide is characterized by peaks whose energies are easily differentiable from energies associated with those due to other possible elements. Also the indicator should be among the most easily detectable of the nuclides formed by the particular element. The presence or absence of all the isotopic spectra due to the element is then decided by the presence or absence of the spectrum due to the indicator nuclide.

The standard spectrum due to the activation of a particular isotope of an element along with all associated information constitutes one library entry. The isotopic entries corresponding to an element are grouped together, the entry of the indicator isotope being first. The program checks for the presence of the indicator spectrum of each element series of entries (which as a special case may contain only one entry if the element has only one activatible isotope). If the indicator spectrum

is absent from the composite spectrum, the search skips to the indicator entry of the next elemental series. If, however, the indicator is present the entire elemental series of isotopic spectra is read from the library tape.

After a standard isotopic spectrum is read from the library, it is expanded or contracted along the abscissa so that its energy scale is equal to that of the composite. At the same time the ordinate values of the standard spectrum are adjusted so that the total number of counts in the spectrum remains the same. The spectrum is then smoothed and stored along with its associated information on an intermediate tape in preparation for stripping.

The program scans the library testing for the presence of each indicator spectrum until the end of the library is reached. At that point the isotopic entries corresponding to all the components detected in the complex spectrum are stored on the intermediate tape and the program is ready to determine the actual amount of each one present in the composite.

Quantitative Analysis

Recall equation 1:

$$F(i) = \sum_{j=1}^{N} a_j f_j(i) \qquad i = 1,2,3,\ldots,M \qquad (1)$$

where, as before, $f_j(i)$ is the j^{th} standard isotopic spectrum, $F(i)$ is the composite spectrum and a_j are the weighting factors of each component spectrum in the composite. Note that there are N component spectra and M channels in each spectrum. As was mentioned the number of equations can be reduced to N to permit a unique algebraic solution. For reasons

to be discussed this is presently the method of quantitative analysis used in this program.

Let the abscissa of the spectrum be divided into N intervals $[i_1,i_2]$, $[i_2,i_3]$, . . . , $[i_k,i_{k+1}]$, . . . , $[i_N,i_{N-1}]$. Summing equation 1 over the k^{th} interval yields

$$T_k = \sum_{i=i_k}^{i_{k+1}} F(i) = \sum_{i=i_k}^{i_{k+1}} \left[\sum_{j=1}^{N} a_j f_j(i) \right] . \qquad (6)$$

Define a matrix as follows:

$$g_{kj} = \frac{\text{counts in } k^{th} \text{ interval of } j^{th} \text{ standard spectrum}}{\text{total counts in } j^{th} \text{ standard spectrum}}$$

that is,

$$g_{kj} = \frac{\sum_{i=i_k}^{i_{k+1}} f_j(i)}{\sum_{i=1}^{M} f_j(i)} . \qquad (7)$$

Since the a_j's are constants with respect to i,

$$g_{kj} = \frac{\sum_{i=i_k}^{i_{k+1}} a_j f_j(i)}{\sum_{i=1}^{M} a_j f_j(i)}$$

or

$$\sum_{i=i_k}^{i_{k+1}} a_j f_j(i) = g_{kj} \sum_{k=1}^{M} a_j f_j(i) . \qquad (8)$$

Then reversing the order of summation in equation 6 and substituting equation 8, yields:

$$T_k = \sum_{j=1}^{N} g_{kj} \sum_{i=1}^{M} a_j f_j(i) \quad . \tag{9}$$

Letting

$$H_j = \sum_{i=1}^{M} a_j f_j(i) \quad , \tag{10}$$

equation 9 becomes

$$T_k = \sum_{j=1}^{N} g_{kj} H_j \quad . \tag{11}$$

Notice that with the information given (the composite spectrum and the N standard isotopic spectra) T_k and g_{kj} defined by equation 6 and 7 are known quantities. Equation 11 is therefore a set of N equations in the N unknowns H_j. From equation 10,

$$a_j = \frac{H_j}{\sum_{i=1}^{M} f_j(i)} \tag{12}$$

and letting

$$S_j = \sum_{i=1}^{M} f_j(i) \tag{13}$$

where S_j is the total counts in the j^{th} standard spectrum (a known quantity), equation 12 becomes

$$a_j = \frac{H_j}{S_j} . \qquad (14)$$

In looking at this method of analysis notice that the coefficient matrix which is defined by equation 7 is of such a simple nature that each component of the matrix can be calculated with only a small fraction of the total spectral data (composite and N standards) immediately available. This means that spectra with a relatively large number of channels (e.g., 1024) can be used without running out of core storage in the computer. Using this method a 1024 channel complex spectrum containing 20 components can be analyzed using only about 2500 words of spectrum and equation working storage.

This approach permits the use of a large number of channels in the qualitative analysis while in effect reducing the number of channels for quantitative analysis. As will be discussed later, however, considerable accuracy is still attained in calculating the values of the a_j's.

Starting on the least squares approach (equation 4) it can be shown[3] that the coefficient matrix of the set of N equations resulting is of the form

$$h_{kj} = \sum_{i=1}^{M} \left[\frac{f_j(i) f_k(i)}{F(i)} \right] \qquad (15)$$

Notice that it is necessary to have the composite spectrum and all N standard spectra in core storage at one time in order to calculate these coefficients. Thus analysis of a 1024 channel, 20 component spectrum would require about 22,000 words of working storage which is far beyond the capacity of the system now in use. For this reason programs using this method are much more seriously limited as to

numbers of channels and components although for certain applications least squares is still the best procedure.

The set of equations (equation 11) once set up could be solved by any of several methods. Since, however, each set is solved only once for a given coefficient matrix g_{kj}, it was decided to use matrix triangularization and back substitution.[12]

Having solved the set of equations for H_j's there remains only the calculation of the amounts of the corresponding isotopes and hence elements in the sample of material being analyzed. Details of the calculation of sample composition may be found in Appendix C.

RESULTS

The program just described has been under development for about eight months and is at this point approximately half finished.

The parts of the program dealing with the preliminary processing of spectra are largely finished. As a test of the data smoothing, a 1024 channel spectrum was given a 5-, 7-, and 9-point smoothing convolution using a quadratic-cubic fit. The results were very good, so good in fact that the statistical peak validity tests will probably have to be changed somewhat. Figure 2 shows the top of a peak before and after a 9-point convolution.

As can be seen the shape is considerably improved. The quadratic-cubic fit attempts to make the top of the peak parabolic which is close to the theoretical peak shape (approximately Gaussian). A fit over fewer points tends to retain more fluctuations, however as the number of points increases small but significant peaks tend to be flattened.

The peak detection and location procedure was originally designed for unsmoothed data. As a test of a 256 channel unsmoothed spectrum was processed for peak detection and location with the following values of parameters: $p = 3$, $h = 50$, $g = 4$. The results for several peaks in the spectrum are shown in Figure 3. As can be seen the center locations seem to be reasonably accurate. It was found that the peak detection was quite reliable in that no significant peaks were overlooked and yet all peaks detected were genuine.

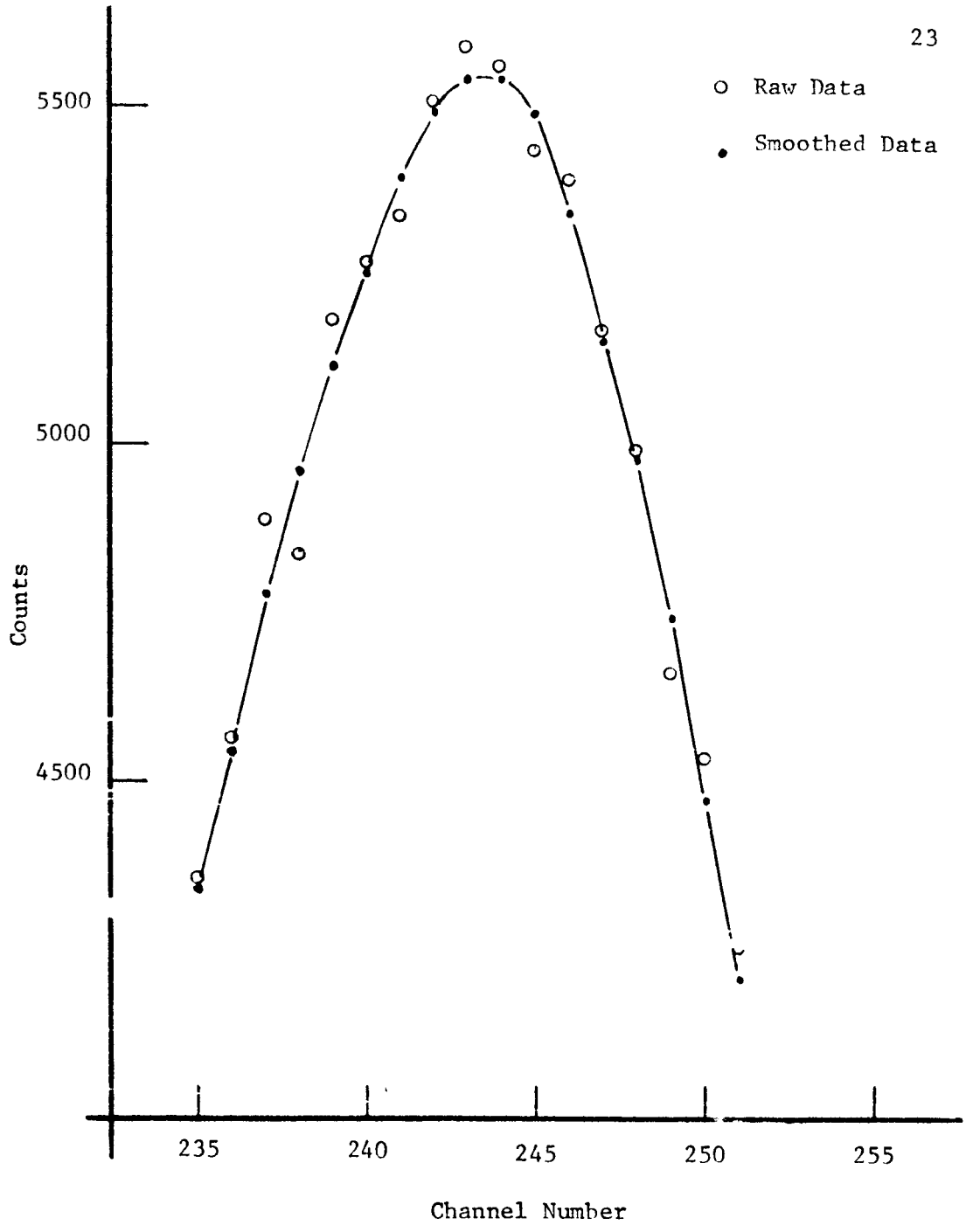


Figure 2

Top of Peak in Spectrum Before and After a 9-Point Quadratic-Cubic Convolution.

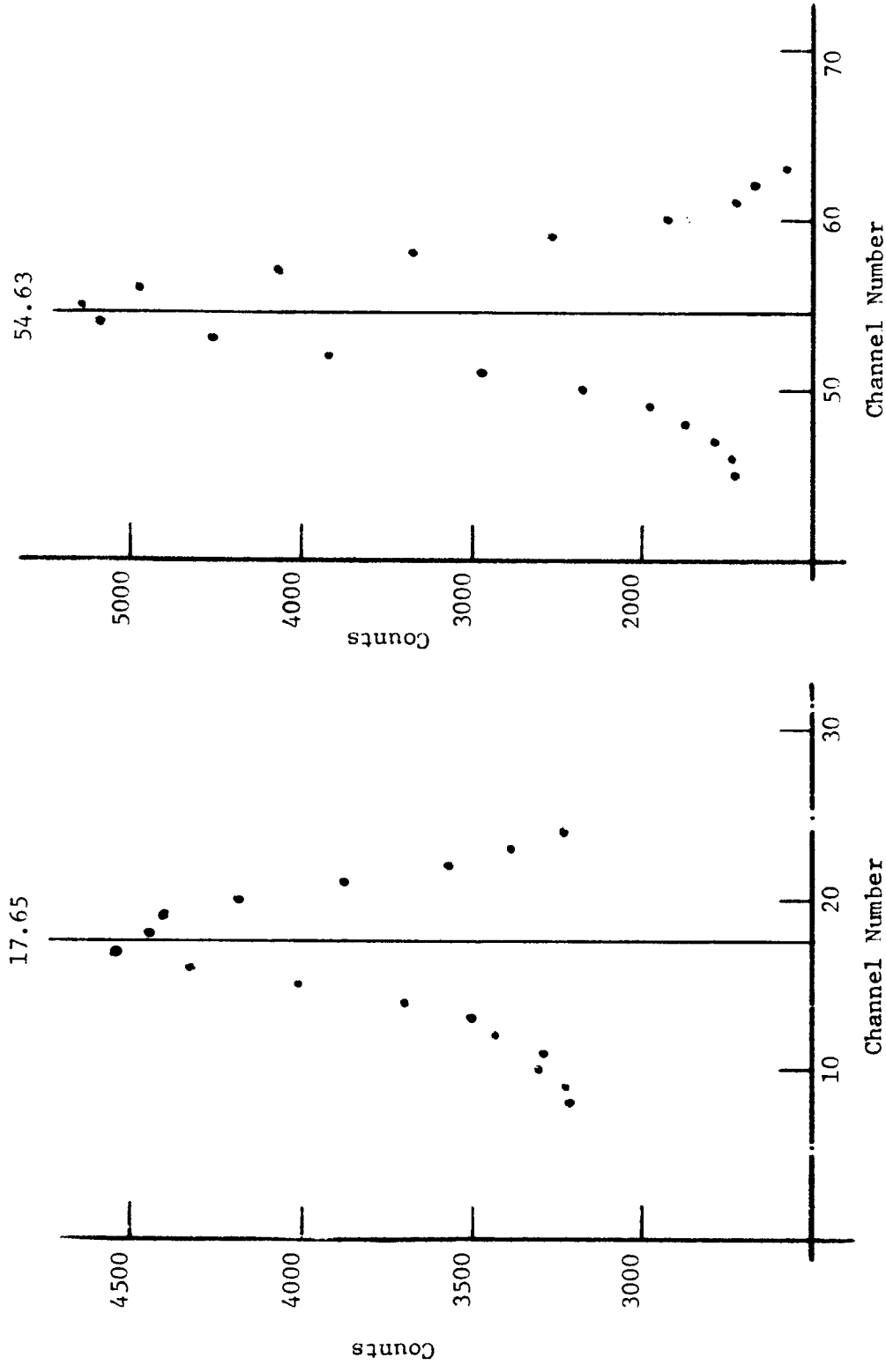


Figure 3

Computer Location of Peaks

To test the energy calibration procedure, three gamma standard spectra (Cs^{137}, Na^{22}, and Co^{60}) were read in along with the standard peak energies and approximate peak locations. Table 1 shows a summary of the output and Figure 4 shows the corresponding graph of energy with channel number. In general the accuracy of the resulting energy-channel number ratio was much better than could be attained manually.

The qualitative analysis section is the least developed part of the program at this point. It is still in the early stages; no results have yet been obtained.

The quantitative part of the analysis has been the object of most of the work done on this program to date but even so, due to the complexities of the problem, no formal results have been obtained. However, on the basis of preliminary tests it has been found that errors on the order of 1 to 2% may be expected in the values of the a_j's produced by the method of stripping described previously. Also, it has been found that the error in the solution of the set of algebraic equations (equation 11) is several orders of magnitude smaller than 1% and so need not be considered.

In summary, the preliminary spectrum processing section is almost complete and produces highly acceptable results. The component identification section is not yet far enough along to produce any results. The quantitative analysis (stripping) section is still under development, but early tests show that the method works and should produce acceptable results.

Standard Peaks as Processed

isotope	peak energy (MeV)	location read in (channel no.)	location used by program (channel no.)
C_s^{137}	0.66	55	54.69
N_a^{22}	0.51 1.28	43 104	42.56 104.52
C_o^{60}	1.17 1.33	97 110	96.61 109.10

Energy Scale = 1.217×10^{-2} MeV/channel

Table 1

Summary of Energy Calibration Output

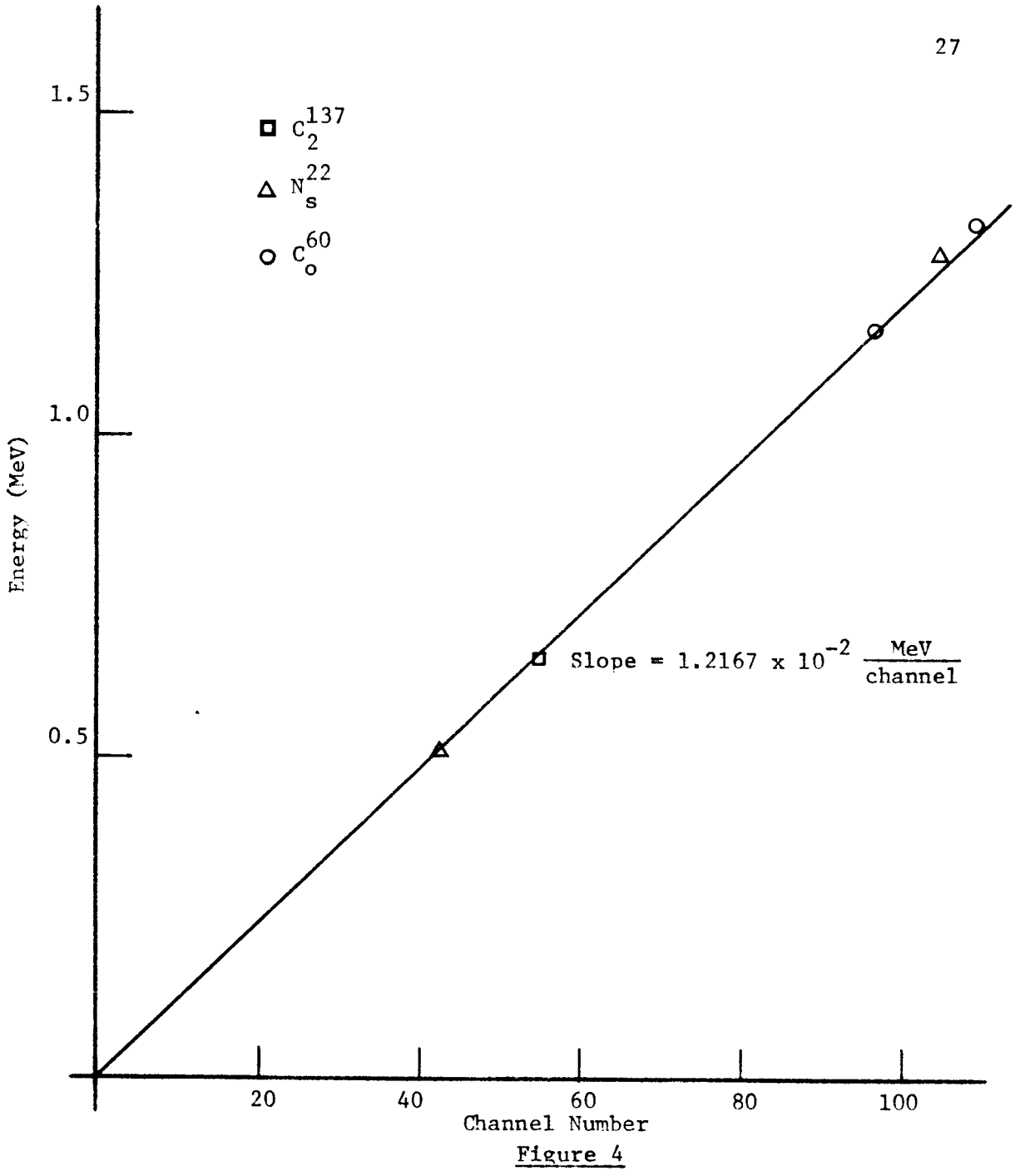


Figure 4

Graph of Energy v.s. Channel Number as Calculated by Program using Gamma Standards.

CONCLUSIONS

On the basis of the results achieved up to this time some slight changes in method and possible new directions of development are indicated.

Even though the preliminary processing portion of the program is relatively finished there are some small changes planned to further increase the quality of results. First, the method of spectrum first derivative generation will be changed from a 3 point linear fit to a 7 or 9 point quadratic fit. This is expected to increase the accuracy and reliability of peak detection and location. It is also anticipated that this increase in the quality of the derivative will necessitate an additional peak validity test, probably some requirement on the height to width ratio.

As was mentioned, the first rough tests of the stripping procedure indicated errors of 1 to 2%. In tests of least squares stripping,[3] however, errors as small as 0.01% were obtained. Therefore to increase accuracy, the procedure in this program will probably be changed to one in which the number of equations in the N unknowns will not be decreased to N, but to some number between M and N depending on the core storage available after the program is read in and stored. The main limitation on the accuracy of stripping is, therefore, the amount of core storage available in the computer system.

It should also be noted that the present method of stripping requires the standard spectra to be read into core storage from magnetic

tape. For example in the process of stripping 20 components from a composite spectrum, each of the 20 standard spectra must be read from magnetic tape to core twice. If all stripping information could be brought into core at once, much less tape reading would be required with a consequent savings in computer time.

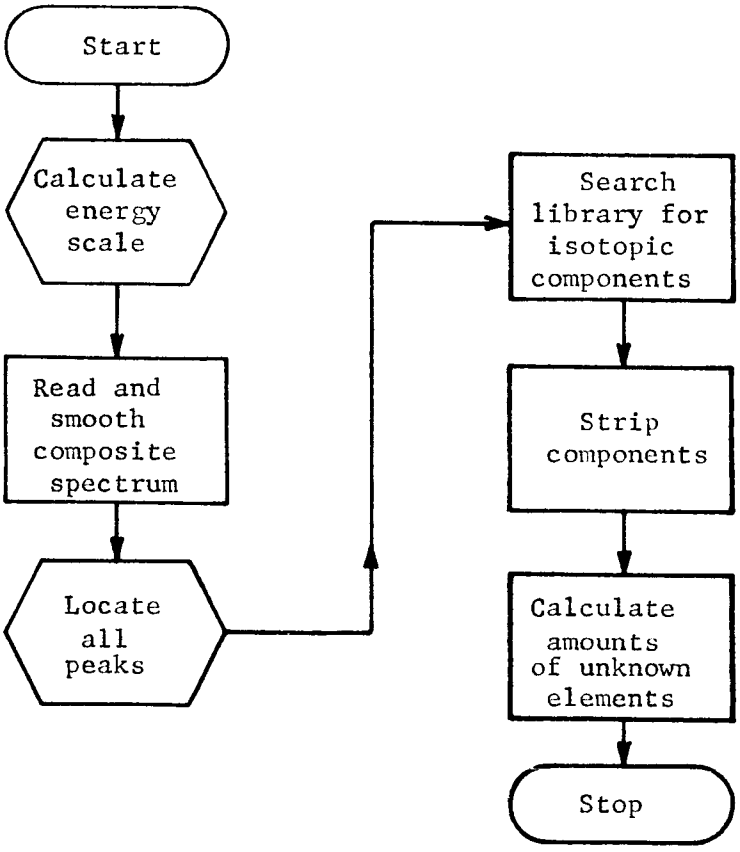
The much larger amount of core storage available on the CDC 6400 system when it becomes operational will permit two important changes in the program which will greatly increase the accuracy and speed of an analysis. First, all storage on intermediate tape can be dispensed with, thus considerably decreasing the amount of computer time per analysis Second, pure least squares can be used in the stripping, thus greatly increasing accuracy.

APPENDIX A

Flowcharts and Program Listings

Included here is a summary flowchart of the program, as well as flowcharts and program listings of a few of the more important subroutines which are reasonably complete and have produced good results.

Summary Flowchart
of Program



Subroutine to Smooth Spectrum

Quadratic - cubic convolution integers (9 points):

$C_1 = C_9 = -21$

$C_2 = C_8 = 14$

$C_3 = C_7 = 39$

$C_4 = C_6 = 54$

$C_5 = 59$

$N = 231$

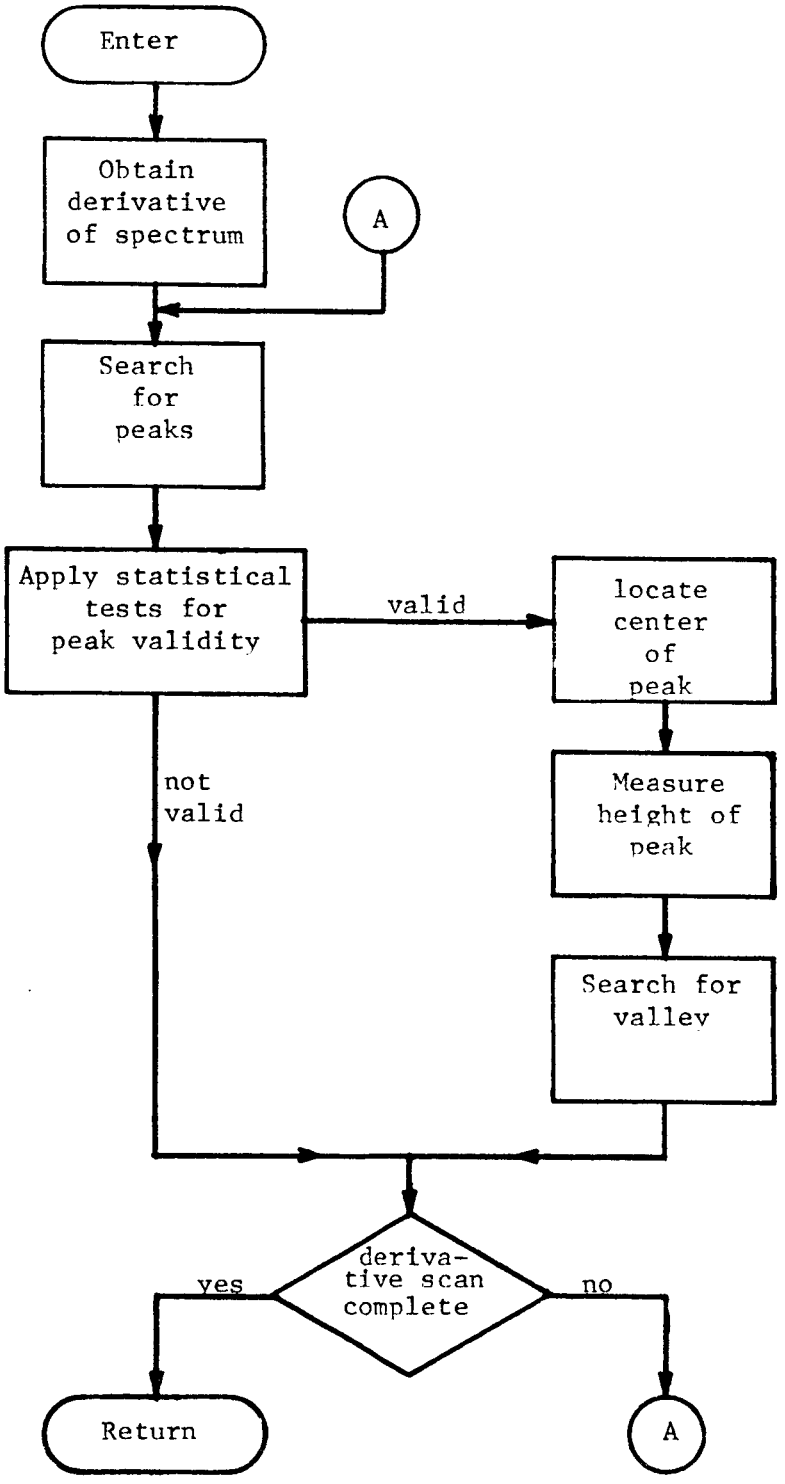
Variable listing for program

M = number of channels in program

SPEC(I) = count in I^{th} channel of spectrum

```
C       SUBROUTINE TO SMOOTH SPECTRUM USING QUADRATIC-CUBIC
C       LEAST SQUARES FIT DATA CONVOLUTION (9 POINTS)
        SUBROUTINE SMOT9(M,SPEC)
        DIMENSION SPEC(1024),AXE(9)
C       INITIALIZE
        DO 2 J=1,9
      2 AXE(J)=SPEC(J)
C       SMOOTH
        NUTS=M-5
        DO 4 I=5,NUTS
        SPEC(I)=(-21.0*(AXE(1)+AXE(9))+14.0*(AXE(2)+AXE(8))+
       1 39.0*(AXE(3)+AXE(7))+54.0*(AXE(4)+AXE(6))+59.0*AXE(5)
       2 )/231.0
        DO 6 J=1,8
      6 AXE(J)=AXE(J+1)
      4 AXE(9)=SPEC(I+5)
        RETURN
        END
```

Locate Peaks



Subroutine to Locate Peaks

Variable listing for program:

M = number of channels in spectrum

NUM = number of peaks found

AMX = count at top of peak

AMN = count at previous minimum

NRES = minimum number of consecutive channels of same sign to indicate sign change in derivative (p)

HI = minimum peak height relative to previous minimum (h)

NCEN = radius of area centered on peak used to determine center of peak (g)

AX(I) = count at I^{th} channel of spectrum

AY(I) = derivative of spectrum at I^{th} channel

PEAK(J) = location of J^{th} peak detected

HITE(J) = relative height of J^{th} peak detected

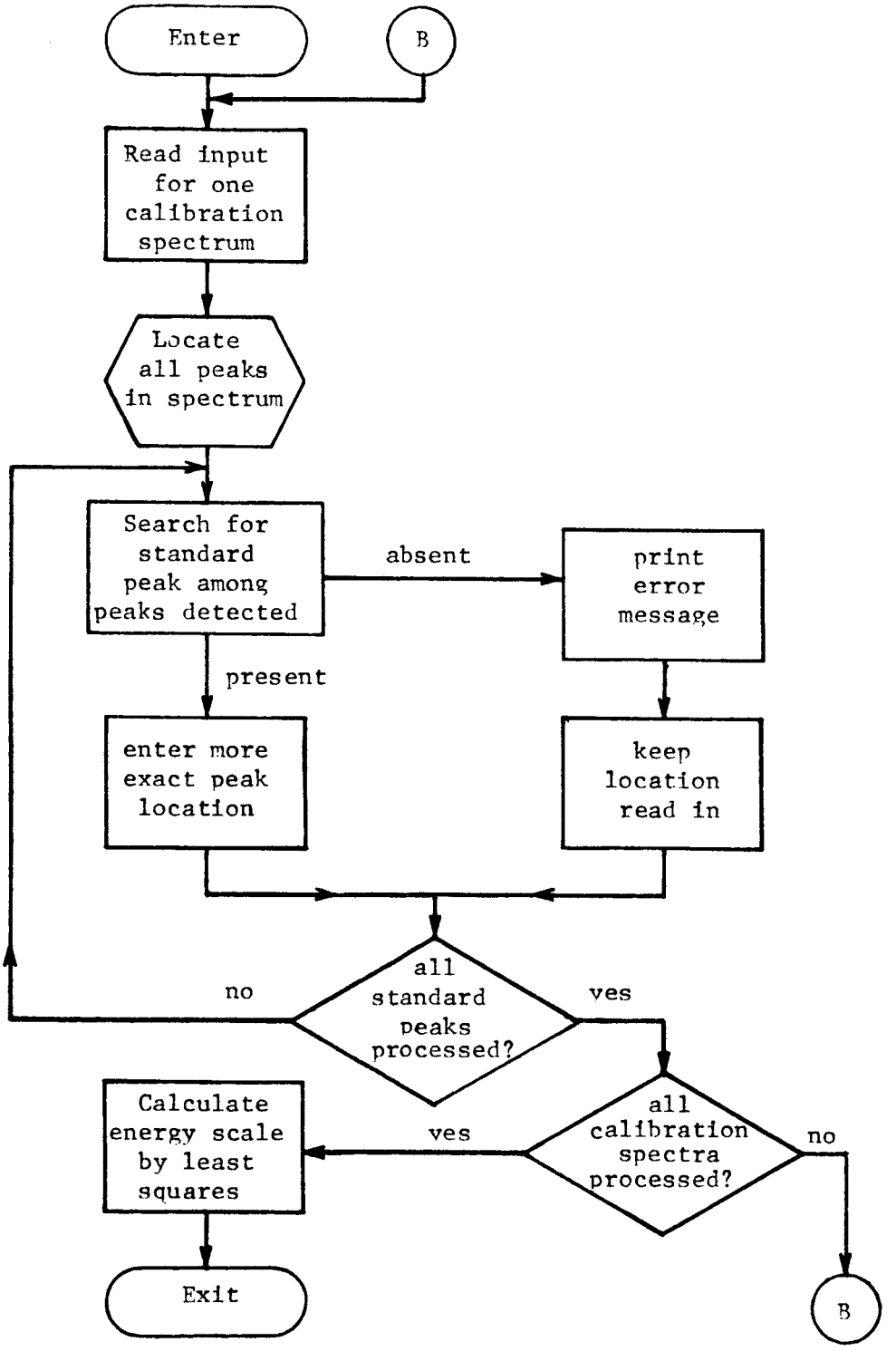
K: search index

K = 1: search for peak

K = 2: search for valley

```
C       SUBROUTINE TO LOCATE ALL IMPORTANT PEAKS IN SPECTRUM
        SUBROUTINE LOC(M,AX,NUM,PEAK,HITE,AY)
        DIMENSION AX(1024),AY(1056),PEAK(100),HITE(100)
C       ESTABLISH PARAMETERS
        HI=20.0
        NRES=3
        NCEN=M/64
C       OBTAIN DERIVATIVE
        CALL DERIV(M,AX,AY)
        NUM=0
        K=1
        AMN=0.0
        MM=M-NCEN
C       SCAN DERIVATIVE TO LOCATE PEAKS
        DO 2 I=4,MM
      8 GO TO(10,12),K
C       SEARCH FOR MAXIMUM
     10 DO 14 J=1,NRES
        NAT=I+J-1
        IF(AY(NAT))14,2,2
     14 CONTINUE
        AMX=(AX(I-1)+AX(I))/2.0
        IF(AMX-AMN-HI) 2,18,18
     18 NUM=NUM+1
C       CALCULATE RELATIVE HEIGHT OF PEAK
        HITE(NUM)=AMX-AMN
C       CALCULATE CENTER OF PEAK
        SUMXY=0.0
        SUMX=0.0
        SUMY=0.0
        SUMX2=0.0
        N=2*NCEN
        DO 20 J=1,N
        NUTS=I-NCEN+J-1
        SUMXY=SUMXY+FLOTF(NUTS)*AY(NUTS)
        SUMX=SUMX+FLOTF(NUTS)
        SUMY=SUMY+AY(NUTS)
     20 SUMX2=SUMX2+FLOTF(NUTS)**2
        PEAK(NUM)=(SUMXY*SUMX-SUMY*SUMX2)/(FLOTF(N)*SUMXY-SUMX
       1 *SUMY)
        K=2
        GO TO 2
C       SEARCH FOR MINIMUM
     12 DO 22 J=1,NRES
        NAT=I+J-1
        IF(AY(NAT))2,2,22
     22 CONTINUE
        AMN=(AX(I-1)+AX(I))/2.0
        K=1
      2 CONTINUE
        RETURN
        END
```

Calculate Energy Scale



Subroutine to Calculate Energy Scale

Variable listing for program:

YK = energy per channel (k in text)

M = number of channels in calibration spectra

NCAL = total number of calibration spectra to be read in

KAP = number of standard peaks in calibration spectrum being processed

LKAP = total number of standard peaks in all calibration spectra processed

NUM = total number of peaks detected in calibration spectrum being processed.

STAN(1,I) = location of I^{th} standard peak

STAN(2,I) = energy (MeV) of I^{th} standard peak

PEAK(K) = location calculated for K^{th} peak detected

HITE(K) = relative height of K^{th} peak detected

AX(J) = count in J^{th} channel of calibration spectrum being processed

```
C       SUBROUTINE TO DETERMINE ENERGY SCALE
C       FROM CALIBRATION SPECTRA
        SUBROUTINE SCALE(YK)
        DIMENSION STAN(2,30),PEAK(100),AX(1024),NSTAN(10),
       1 NAME(16)
    51 FORMAT(///65H **** DETERMINATION OF ENERGY SCALE FROM
      1CALIBRATION SPECTRA ****)
        PRINT 51
     2 FORMAT(I4/I2)
        READ 2,M,NCAL
        LKAP=0.0
        DO 1 J=1,NCAL
C       J TH SPECTRUM READ AND PROCESSED
        READ 35,(NAME(NZ),NZ=1,16)
    35 FORMAT(16A5)
    37 FORMAT(///,1X,16A5)
        PRINT 37,(NAME(NZ),NZ=1,16)
        READ 6,KAP
     6 FORMAT(I2)
        DO 3 I=1,KAP
        NUTS=LKAP+I
     5 FORMAT(F4.0,6X,F8.6)
        READ 5,STAN(1,NUTS),STAN(2,NUTS)
     3 NSTAN(I)=XFIXF(STAN(1,NUTS))
        LKAP=LKAP+KAP
C       READ IN CALIBRATION SPECTRUM AND SCAN FOR PEAKS
        CALL RD(AX)
        CALL LOC(M,AX,NUM,PEAK)
C       SEARCH FOR STANDARD PEAKS
        NUTS=LKAP-KAP+1
        DO 8 I=NUTS,LKAP
        DO 10 K=1,NUM
        IF(STAN(1,I)-(PEAK(K)-2.0))10,12,12
    12 IF(STAN(1,I)-(PEAK(K)+2.0))14,14,10
    14 STAN(1,I)=PEAK(K)
        GO TO 8
    10 CONTINUE
        MP=I-(LKAP-KAP)
    16 FORMAT(    /13H PEAK NUMBER ,I2,32H OF CALIBRATION SPEC
      1TRUM NUMBER ,I2,21H COULD NOT BE LOCATED/38H LOCATION
      2READ IN USED FOR CALIBRATION)
        PRINT 16,MP,J
     8 CONTINUE
C       PRINT OUTPUT
    21 FORMAT(  /32H CHANNEL NOS. OF PEAKS DETECTED*,//,
      1(10F10.2,/))
        PRINT 21,(PEAK(JZ),JZ=1,NUM)
    25 FORMAT(///61H STANDARD PEAKS AS PROCESSED FOR CALIBRAT
      1ION SPECTRUM NUMBER ,I2,//28H ENERGY   LOCATION  LOCAT
      2ION,/26H  (MEV)    READ IN     USED,//)
        PRINT 25,J
    27 FORMAT(F6.2,5X,I4,F12.2,/)
```

```
      DO 29 KK=1,KAP
      KQ=LKAP-KAP+KK
   29 PRINT 27,STAN(2,KQ),NSTAN(KK),STAN(1,KQ)
    1 CONTINUE
C     CALCULATE ENERGY SCALE BY LEAST SQUARES
      SUME2=0.0
      SUMEX=0.0
      DO 18 I=1,LKAP
      SUME2=SUME2+STAN(2,I)**2
   18 SUMEX=SUMEX+STAN(2,I)*STAN(1,I)
      YK=SUME2/SUMEX
   41 FORMAT(////,15H ENERGY SCALE =,1PE14.7,16H MEV PER CHA
     1NNEL,///)
      PRINT 41,YK
      RETURN
      END
```

Subroutine to Strip Components

Variable listing for program:

M = number of channels in composite spectrum

N = number of components in composite spectrum

MIN to MAX = range of channels in composite spectrum actually used for stripping

AC = total number of counts in composite spectrum

H(J) = total number of counts in J^{th} component spectrum (H_j)

T(K) = total number of counts in K^{th} interval of component spectrum

TOT(J) = total number of counts in J^{th} standard isotopic spectrum (S_j)

AX(I) = count in I^{th} channel of composite spectrum (F(i))

AY(I) = count in I^{th} channel of standard spectrum

G(K,J) = matrix component (g_{kj})

CR(J) = weighting factor of J^{th} component (a_j)

```
C       SUBROUTINE TO STRIP N COMPONENTS FROM COMPOSITE
C       SPECTRUM AND DETERMINE AMOUNTS PRESENT
        SUBROUTINE STRIP(AX,N,M,CR,MIN,MAX)
        DIMENSION AX(1024),AY(1056),T(20),G(20,20),CR(20),
C      1 H(20),TOT(20)
        COMMON AY
C       CALCULATE SIZE OF INTERVAL
        MDEL=(MAX-MIN)/N
C       CORRECT MAX FOR TRUNCATION
        MAX=MDEL*N+MIN
C       DETERMINE COUNTS IN I TH INTERVAL OF COMPOSITE
C       SPECTRUM
        DO 2 I=1,N
        T(I)=0.0
        DO 2 J=1,MDEL
        NUTS=MIN+(I-1)*MDEL+J
      2 T(I)=T(I)+AX(NUTS)
C       PROCESS J TH STANDARD SPECTRUM
        REWIND 3
        DO 4 J=1,N
        READ TAPE 3,AY
C       DETERMINE COUNTS IN J TH STANDARD
C       SPECTRUM (MIN TO MAX)
        TOT(J)=0.0
        NUTS=MIN+1
        DO 6 I=NUTS,MAX
      6 TOT(J)=TOT(J)+AY(I)
        DO 4 I=1,N
C       CALCULATE COUNTS IN I TH INTERVAL OF J TH STANDARD
C       SPECTRUM
        PART=0.0
        DO 8 K=1,MDEL
        NUTS=MIN+(I-1)*MDEL+K
      8 PART=PART+AY(NUTS)
C       CALCULATE (I,J) TH COMPONENT OF COEFFICIENT MATRIX
      4 G(I,J)=PART/TOT(J)
C       OBTAIN SOLUTION OF SYSTEM OF EQUATIONS
        CALL SYMEQ(G,H,T,N)
        REWIND 3
        DO 10 J=1,N
C       OBTAIN RATIO OF COUNTS IN J TH COMPONENT (MIN TO MAX)
C       TO COUNTS IN J TH STANDARD SPECTRUM (MIN TO MAX)
        CR(J)=H(J)/TOT(J)
C       STRIP J TH COMPONENT OUT OF COMPOSITE
        READ TAPE 3,AY
        DO 10 I=1,M
     10 AX(I)=AX(I)-AY(I)*CR(J)
        RETURN
        END
```

APPENDIX B

Spectral Library Format

The standard isotopic spectral library consists of a series of nonformated records on magnetic tape. Each record contains one isotopic spectrum along with all related information and has a length of 1080 words. Each of these records or entries is characterized by an entry number which is the first word in the record. The end of the library is signified by the number 999.0 stored after the end of the last entry.

The following is a list of the information stored in one library entry along with relative locations within the tape record

1. Entry number (1)
2. Name of element (2 - 4)
3. Mass number of isotope (5)
4. Number of standard peaks (6)
5. Energies of standard peaks (7-11)
6. Relative heights of standard peaks (12-16)
7. Energy scale (MeV/channel) (17)
8. Decay constant (18)
9. Mass of sample of standard element (19)
10. Fractional abundance of isotope (20)
11. Number of isotopes in library of this element (21)
12. Entry numbers of other isotopes of this element (22 - 31)
13. Irradiation time (32)

14. Time count started (33)

15. Time count stopped (34)

16. Reactor power during irradiation (35)

17. Number of channels in standard spectrum (56)

18. Standard spectrum (57 - 1080)

When the program tests for the presence of an isotope, it reads only through item 11 in the corresponding library entry. If the test is positive, the tape is backspaced and the entire entry read off. This is done to avoid wasting time reading unnecessary spectra from the library tape.

APPENDIX C

Summary of Calculation of Sample Composition

Let $\dot{H}_j(t)$ be the count rate due to the j^{th} component isotope in the sample at time, t, after the end of irradiation. Similarly, define $\dot{S}_j(t)$ to be the count rate due to the j^{th} isotope in the known standard element sample (used to make the j^{th} standard library spectrum) at time, t, after end of irradiation. Then if t_1 and t_2 are the times the count is started and stopped after end of irradiation of sample,

$$H_j = \int_{t_1}^{t_2} \dot{H}_j(t)\, dt$$

$$= \int_{t_1}^{t_2} \dot{H}_j(0) \exp(-\lambda_j t)\, dt.$$

Integrating,

$$H_j = \frac{\dot{H}_j(0)}{\lambda_j} \left[\exp(-\lambda_j t_1) - \exp(-\lambda_j t_2)\right],$$

and solving for $\dot{H}_j(0)$ yields

$$\dot{H}_j(0) = \frac{\lambda_j H_j}{\left[\exp(-\lambda_j t_1) - \exp(-\lambda_j t_2)\right]} \qquad (1c)$$

Similarly, for $\dot{S}_j(0)$, if t_{1s} and t_{2s}, the count start and stop times after end of irradiation of standard,

$$\dot{S}_j(0) = \frac{\lambda_j S_j}{[\exp(-\lambda_j t_{1s}) - \exp(-\lambda_j t_{2s})]} \quad . \tag{2c}$$

Equations 1c and 2c correct the count for decay of the sample between irradiation and counting and during the count itself.

If the sample is irradiated for a time, T, in a thermal neutron flux Φ,

$$\dot{H}_j(0) = \frac{W_j N_A \sigma_j \Phi}{A_j} [1 - \exp(-\lambda_j T)] \tag{3c}$$

where

W_j = mass of j^{th} isotope in sample (grams)

N_A = Avagadro's number (number of atoms per gram-atom)

σ_j = thermal activation cross section of j^{th} isotope

A_j = mass number of j^{th} isotope

Similarly, if the standard sample is irradiated for a time, T_s, in a flux Φ_s,

$$\dot{S}_j(0) = \frac{W_{js} N_A \sigma_j \Phi_s}{A_j} [1 - \exp(-\lambda_j T_s)] \tag{4c}$$

where the subscript, s, indicates the standard element sample.

Dividing equation 3c by equation 4c and solving for W_j yields:

$$W_j = S_j \left[\frac{\dot{H}_j(0)}{\dot{S}_j(0)}\right] \left\{\frac{[1 - \exp(-\lambda_j T_s)]}{[1 - \exp(-\lambda_j T)]}\right\} \left[\frac{\Phi_s}{\Phi}\right] \tag{5c}$$

where from equations 1c and 2c,

$$\frac{\dot{H}_j(0)}{\dot{S}_j(0)} = \left[\frac{H_j}{S_j}\right] \left\{ \frac{[\exp(-\lambda_j t_{1s}) - \exp(-\lambda_j t_{2s})]}{[\exp(-\lambda_j t_1) - \exp(-\lambda_j t_2)]} \right\} . \quad (6c)$$

Notice that

$$\left[\frac{H_j}{S_j}\right] = a_j \quad (7c)$$

where a_j was the number resulting from the gamma spectroanalysis.

Therefore, using equations 5c and 6c along with the results of the analysis of the composite spectrum, the isotopic composition of the sample may easily be calculated. Notice also that if the fractional isotopic abundances in the unknown sample are normal, the procedure will also yield the elemental composition.

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